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VERIFICATION OF TRANSLATION

Assistant Commissioner of Patents
Washington, DC 20231

Sir:

I, Takahiko MIZOBE, Chartered Patent Attorney of Furuya & Co., located at 6th Floor, Hamacho-Hanacho Building, 2-17-8, Nihonbashi-Hamacho, Chuo-ku, Tokyo 103-0007, Japan, declare that:

1. I am well acquainted with the Japanese and English languages;
2. I verified the translation of the above-identified non-provisional patent application from Japanese to English language; and
3. The hereto-attached English translation is a full, true and correct translation of the above-identified non-provisional patent application to the best of my knowledge and belief.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated: September 9, 2003 _Takahiko Mizobe_

Takahiko MIZOBE

02075US
non-provisional

Description

GAS GENERATING COMPOSITION

Technical Field

The present invention relates to a gas generating composition suitable for an air bag restraining system of automobiles and the like, its molded article and an inflator for an air bag using the same.

Background Art

As a gas generating agent for an air bag as a passenger-protecting system in automobiles, a composition using sodium azide has been often used so far. However, a toxicity to human bodies [LD_{50} (oral-rat) = 27 mg/kg] or hazard in handling of sodium azide has been regarded as a serious problem. Therefore, as safe non-azide based gas generating compositions, gas generating compositions containing various nitrogen-containing organic compounds have been developed to replace the above composition.

US-A 4,909,549 discloses a composition comprising hydrogen-containing tetrazole or triazole compounds and an oxygen-containing oxidizing agent. US-B 4,370,181 discloses a gas generating composition comprising a hydrogen-free bitetrazole metal salt and an oxygen-free oxidizing agent. US-B 4,369,079 discloses a gas generating composition comprising a hydrogen-free bitetrazole metal salt and an alkali metal nitrate, an alkali metal nitrite, an alkaline earth metal

nitrate, an alkaline earth metal nitrite or a mixture thereof. US-B 5,542,999 discloses a gas generating agent comprising a fuel such as GZT, TAGN (triaminonitroguanidine), NG (nitroguanidine), NTO, copper oxide, a catalyst for reducing toxic gases and a coolant. JP-A 10-72273 discloses a gas generating agent comprising a bitetrazole metal salt, a bitetrazole ammonium salt or aminotetrazole and ammonium nitrate.

In the non-azide based gas generating compositions described above, however, nitrogen is often contained in a fuel and/or an oxidizing agent, and thus generation of carbon monoxide, nitrogen oxides and ammonia after combustion is hardly suppressed at low levels.

Disclosure of the Invention

Accordingly, a purpose of the invention is to provide a gas generating composition which is restrained from generating carbon monoxide and nitrogen oxides, is further restrained from generating ammonia and is good in a combustion stability and safe at the time of handling and then a molded article thereof and an inflator for an air bag using the same.

The invention provides a gas generating composition comprising the following components (a) and (b):

(a) a polyoxymethylene polymer or a polyoxymethylene copolymer as fuel and

(b) a nitrogen-free oxidizing agent.

Further, the invention provides a molded article in the form of a single-perforated cylinder, a perforated (porous)

cylinder or pellets obtained from the gas generating composition. The single-perforation or perforation may or may be a through-hole or a hollow.

Still further, the invention provides an inflator for an air bag using the gas generating composition or the molded article.

The gas generating composition and its molded article of the invention are easy to handle because of a low toxicity and less hazard. Moreover, an amount of carbon monoxide to be generated at the time of combustion is low, and no nitrogen oxides and ammonia are formed.

Embodiments of the Invention

The polyoxymethylene polymer or polyoxymethylene copolymer used as the component (a) in the invention is low in toxicity, and when combined with the component (b), it shows a lower combustion temperature and a higher burning rate.

As the component (a), paraformaldehyde or polyacetal resin is preferable because LD_{50} (oral-rat) is 800 mg/kg to be safe at the time of handling, and the cost is low.

The oxidizing agent used as the component (b) in the invention is at least one selected from the group consisting of copper oxide, iron oxide, molybdenum oxide, cobalt oxide, potassium perchlorate, potassium chlorate, manganese dioxide, strontium peroxide, potassium permanganate, barium peroxide and the like, among which copper oxide is preferable.

When the gas generating composition of the invention is

in a two-component system consisting of the components (a) and (b), the content of the component (a) is preferably 5 to 50 mass %, more preferably 5 to 35 mass %. The content of the component (b) is preferably 95 to 50 mass %, more preferably 95 to 65 mass %.

A preferable example of the gas generating composition in a two-component system is a composition comprising (a) paraformaldehyde and (b) copper oxide. In this case, the content of (a) paraformaldehyde is preferably 5 to 35 mass % and the content of (b) copper oxide is preferably 95 to 65 mass %.

Another preferable example of the gas generating composition in a two-component system is a composition comprising (a) polyacetal resin and (b) copper oxide. In this case, the content of (a) polyacetal resin is preferably 5 to 35 mass % and the content of (b) copper oxide is preferably 95 to 65 mass %.

When the gas generating composition of the invention is in a two-component system consisting of the components (a) and (b) or in a three-component system consisting of the components (a), (b) and (d), its molded article may, if poor in molding strength, collapse upon actual combustion and burn too acceleratedly to make control of combustion impossible. Accordingly, the binder as the component (c) is preferably added.

The binder as the component (c) is at least one selected from the group consisting of carboxymethylcellulose (CMC), sodium carboxymethylcellulose (CMCNa), potassium carboxymethylcellulose, cellulose acetate, cellulose acetate

butyrate (CAB), methyl cellulose (MC), ethyl cellulose (EC), hydroxyethyl cellulose (HEC), ethylhydroxyethyl cellulose (EHEC), hydroxypropyl cellulose (HPC), carboxymethylethyl cellulose (CMEC), fine crystalline cellulose, polyvinyl alcohol, acrylic rubber, guar gum, starch and silicone. Among these, sodium carboyxmethylcellulose (CMCNa) and guar gum are preferable in view of stickiness, cost and ignitability of the binder.

When the gas generating composition of the invention is in a two-component system of the components (a) and (b) or in a three-component system of the components (a), (b) and (c), the additive as the component (d) is preferably added for the purpose of regulating the burning rate of the gas generating agent.

The additive as the component (d) is at least one selected from the group consisting of a metal oxide such as cupric oxide, iron oxide, zinc oxide, cobalt oxide, manganese oxide, molybdenum oxide, nickel oxide, bismuth oxide, silica or alumina, a metal hydroxide such as aluminum hydroxide, cobalt hydroxide or iron hydroxide, a metal carbonate or a basic metal carbonate such as cobalt carbonate, calcium carbonate, a basic zinc carbonate or a basic copper carbonate, a composite compound of a metal oxide or a metal hydroxide such as Japanese acid clay, kaolin, talc, bentonite, diatomaceous earth or hydrotalcite, a metal acid salt such as sodium silicate, mica molybdate, cobalt molybdate or ammonium molybdate, silicone, molybdenum disulfide, calcium stearate, silicon nitride and silicon

carbide.

When the amount of generated carbon monoxide is reduced after combustion of the gas generating composition, aluminum hydroxide or cobalt oxide is preferably added as the component (d).

When the gas generating composition of the invention is in a three- or four-component system of the components (a) to (d), the contents of the respective components are as follows: The content of the component (a) is preferably 5 to 35 mass %, more preferably 10 to 25 mass %. The content of the component (b) is preferably 65 to 95 mass %, more preferably 65 to 80 mass %. The content of the component (c) is preferably 0 to 15 mass %, more preferably 1 to 10 mass %. The content of the component (d) is preferably 20 mass % or less, more preferably 3 to 15 mass %.

A preferable example of the gas generating composition in a three-component system is a composition comprising (a) paraformaldehyde, (b) copper oxide and (c) sodium carboxymethylcellulose. In this case, the content of (a) paraformaldehyde is preferably 15 to 25 mass %, the content of (b) copper oxide is preferably 60 to 90 mass %, and the content of (c) sodium carboxymethylcellulose is preferably 0.1 to 10 mass %.

Another preferable example of the gas generating composition in a three-component system is a composition comprising (a) paraformaldehyde, (b) copper oxide and (c) guar gum. In this case, the content of (a) paraformaldehyde is

preferably 15 to 25 mass %, the content of (b) copper oxide is preferably 65 to 90 mass %, and the content of (c) guar gum is preferably 0.1 to 10 mass %.

A still other preferable example of the gas generating composition in a three-component system is a composition comprising (a) polyacetal resin, (b) copper oxide and (c) sodium carboxymethylcellulose or guar gum. In this case, the content of (a) polyacetal resin is preferably 15 to 25 mass %, the content of (b) copper oxide is preferably 65 to 90 mass % and the content of (c) sodium carboxymethylcellulose or guar gum is preferably 0.1 to 10 mass %.

A preferable example of the gas generating composition in a four-component system is a composition comprising (a) paraformaldehyde, (b) copper oxide, (c) sodium carboxymethylcellulose and (d) aluminum hydroxide. In this case, the content of (a) paraformaldehyde is preferably 10 to 25 mass %, the content of (b) copper oxide is preferably 65 to 90 mass %, the content of (c) sodium carboxymethylcellulose is preferably 0.1 to 10 mass % and the content of (d) aluminum hydroxide is preferably 1 to 15 mass %.

Another preferable example of the gas generating composition in a four-component system is a composition comprising (a) polyacetal resin, (b) copper oxide, (c) sodium carboxymethylcellulose and (d) cobalt oxide. In this case, the content of (a) paraformaldehyde is preferably 10 to 25 mass %, the content of (b) copper oxide is preferably 65 to 90 mass %, the content of (c) sodium carboxymethylcellulose is preferably

0.1 to 10 mass % and the content of (d) cobalt oxide is preferably 1 to 15 mass %.

A still other preferable example of the gas generating composition in a four-component system is a composition comprising (a) polyacetal resin, (b) copper oxide, (c) sodium carboxymethylcellulose and (d) aluminum hydroxide. In this case, the content of (a) polyacetal resin is preferably 10 to 25 mass %, the content of (b) copper oxide is preferably 65 to 90 mass %, the content of (c) sodium carboxymethylcellulose is preferably 0.1 to 10 mass % and the content of (d) aluminum hydroxide is preferably 1 to 15 mass %.

A further still other preferable example of the gas generating composition in a four-component system is a composition comprising (a) polyacetal resin, (b) copper oxide, (c) sodium carboxymethylcellulose and (d) cobalt oxide. In this case, the content of (a) polyacetal resin is preferably 10 to 25 mass %, the content of (b) copper oxide is preferably 65 to 90 mass %, the content of (c) sodium carboxymethylcellulose is preferably 0.1 to 10 mass % and the content of (d) cobalt oxide is preferably 1 to 10 mass %.

The gas generating composition of the invention can be molded in a desired shape, and formed into a molded article in the shape of a single-perforated cylinder, a perforated (porous) cylinder or pellets. These molded articles can be produced by a method in which the gas generating composition is added and mixed with water or an organic solvent and the mixture is extrusion-molded (molded articles in the form of a

single-perforated cylinder and a perforated (porous) cylinder) or by a compression-molding method using a pelletizer and the like (molded article in the form of pellets).

The gas generating composition or the molded article obtained therefrom of the invention can be used in, for example, an inflator for an air bag of a driver side, an inflator for an air bag of a passenger side, an inflator for a side air bag, an inflator for an inflatable curtain, an inflator for a knee bolster, an inflator for an inflatable seat belt, an inflator for a tubular system and a gas generator for a pretensioner in various vehicles.

Further, the inflator using the gas generating composition or the molded article obtained therefrom according to the invention may be of a pyrotechnic type in which a gas is supplied only from a gas generating agent or of a hybrid type in which a gas is supplied from both of a compressed gas such as argon and a gas generating agent.

Moreover, the gas generating composition or the molded article obtained therefrom according to the invention can also be used as an igniting agent called an enhancer (or a booster) and the like for transferring energy of a detonator or a squib to a gas generating agent.

Examples

Hereinafter, the invention is illustrated more specifically by referring to the following Examples, but the invention is not limited thereto.

Examples 1 to 2 and Comparative Examples 1 to 2

Gas generating compositions each having a formulation shown in Table 1 were produced. A combustion temperature, a gas output (unit "mol/100 g" indicates the number of mols of a generated gas per 100 g of a composition) and amounts of generated CO and NO of these compositions according to theoretical calculations are shown in Table 1.

Table 1

	formulation (formulation ratio:mass %)	combustion temperature (K)	gas output (mol/100g)	amount of generated CO (mol/100g)	Amount of generated NO (mol/100g)
Example 1	paraformaldehyde/ CuO (15.85/84.15)	1358	1.06	1.2×10^{-4}	0
Example 2	paraformaldehyde/ $KClO_4$ (30.12/69.88)	2847	2.58	1.1×10^{-1}	0
Comparative Example 1	guanidine nitrate/BCN (53.40/46.60)	1780	3.01	3.0×10^{-3}	2.3×10^{-4}
Comparative Example 2	guanidine nitrate/ BCN/guar gum (45.68/51.32/3)	1741	2.87	1.3×10^{-3}	5.8×10^{-5}

BCN: basic copper nitrate

The theoretical amounts of generated NO in Examples 1 to 2 are 0 (zero) which is significantly different from the amounts of generated NO from the non-azide based nitrogen-containing gas generating agents in Comparative Examples 1 to 2.

Examples 3 to 4 and Comparative Examples 3 to 4

Gas generating compositions each having a formulation shown in Table 2 were produced. These compositions were tested

for friction sensitivity and drop hammer sensitivity according to the explosives performance test method of JIS K4810-1979. The results are shown in Table 2.

Table 2

	formulation (formulation ratio:mass %)	friction sensitivity (N)	drop hammer sensitivity (cm)
Example 3	paraformaldehyde/ CuO (15.85/84.15)	>353	>100
Example 4	paraformaldehyde/ CuO/ $KClO_4$ (17.89/72.11/10.00)	>353	>100
Comparative Example 3	guanidine nitrate/BCN (53.40/46.60)	>353	30-40
Comparative Example 4	guanidine nitrate/ BCN/ guar gum (45.68/51.32/3)	>353	60-62

BCN: basic copper nitrate

In Examples 3 to 4, the friction sensitivity exceeds 353N, and the drop hammer sensitivity exceeds 100 cm, and thus the friction drop hammer sensitivity is dull so that the safety in handling is high.

Examples 5 to 6 and Comparative Examples 5 to 6

Gas generating compositions each having a formulation shown in Table 3 were produced. Each of these compositions was molded into a strand, and a pressure index between 4,900 and 8,820 kPa was determined from the following equation: rb = αPn wherein rb is a burning rate, α is a coefficient, P is pressure, and n is a pressure index. The results are shown in Table 3.

Table 3

	formulation (formulation ratio:mass %)	Pressure index
Example 5	paraformaldehyde/ CuO (15.85/84.15)	0.17
Example 6	paraformaldehyde/ CuO/ $KClO_4$ (17.89/72.11/10.00)	0.38
Comparative Example 5	guanidine nitrate/BCN (53.40/46.60)	0.40
Comparative Example 6	Guanidine nitrate/BCN/ guar gum (42.68/52.32/5)	0.20

BCN: basic copper nitrate

The numerical values shown in Examples 5 to 6 reveal reliable burning.

Examples 7 to 8 and Comparative Examples 7 to 8

Gas generating compositions each having a formulation shown in Table 4 were produced, and each of the gas generating compositions was molded into 2 g of a strand. This strand was installed in a sealed bomb having an inner capacity of 1 liter, and the inside of the bomb was purged with nitrogen. Further, the bomb was pressurized up to 6,860 kPa with nitrogen, and the strand was ignited by electrifying a nichrome wire and completely burned. Approximately 20 seconds from the electrofying, a combustion gas was collected in a gas sampling bag, and the concentrations of NO, NO_2, CO and CO_2 were immediately analyzed with a detecting tube. Their values are

shown in Table 4.

Table 4

	formulation (formulation ratio:mass %)	Amount of generated NO(ppm)	amount of generated NO_2(ppm)	amount of generated CO(ppm)	Amount of generated CO_2(ppm)
Example 7	paraformaldehyde/ CuO (15.85/84.15)	0	0	100	3000
Example 8	paraformaldehyde/ $KClO_4$ (30.12/69.88)	0	0	25	7000
Comparative Example 7	guanidine nitrate/BCN (53.40/46.60)	50	0	240	2100
Comparative Example 8	guanidine nitrate/BCN/ guar gum (42.68/52.32/5)	40	0	500	3100

ppm: based on weight

BCN: basic copper nitrate